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Lewis and Brønsted Basicity of Phosphine-Diazomethane Derivatives

Carolin Schneider, James H. W. LaFortune, Rebecca L. Melen,^{b*} and Douglas W. Stephan^{a*}

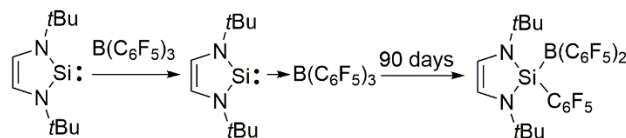
Abstract: The compounds $\text{EtOC(=O)CHNN(PR}_3\text{)}$ ($\text{R} = \text{Ph}$ **1**, Cy **2**, tBu **3**) were prepared via the reactions of the diazomethane and a phosphine. In subsequent reactions with $\text{B(C}_6\text{F}_5\text{)}_3$, the compounds **2** and **3** are shown to exhibit Lewis basicity at the carbonyl oxygen affording $\text{EtOC(=O(B(C}_6\text{F}_5\text{)}_3\text{))CHNNPR}_3$ ($\text{R} = \text{Cy}$ **5**, tBu **6**). Reactions of **5** and **6** with water or phenol, illustrated the Brønsted basicity at the nitrogen atom adjacent phosphorus, affording the compounds, $[\text{EtOC(=O)CHNNHPR}_3][\text{HOB(C}_6\text{F}_5\text{)}_3]$ ($\text{R} = \text{Cy}$ **7**, tBu **8**) and $[\text{EtOC(=O)CHNNHPR}_3][\text{PhOB(C}_6\text{F}_5\text{)}_3]$ ($\text{R} = \text{Cy}$ **9**, tBu **10**), respectively. The formulation of these products is confirmed via spectroscopic and crystallographic studies, and insight is garnered from computations.

Introduction

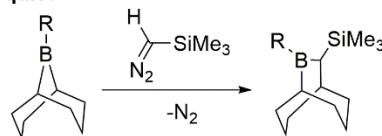
The reactions of frustrated Lewis pairs (FLPs) with small molecules has emerged as a strategy for reactivity.¹⁻⁸ While this work was initiated by the finding that combinations of Lewis acids and bases could activate H_2 ,⁹ this has expanded to encompass a wide range of small molecules including olefins,¹⁰ alkynes,¹¹⁻¹² disulfides,¹³ N_2O ,¹⁴⁻¹⁵ cyclopropanes,¹⁶ CO_2 ,¹⁷⁻¹⁸ CO ,¹⁹⁻²⁰ NO ,²¹ SO_2 ,²²⁻²³ and RNSO .²⁴ Such broad reactivity with substrates typically activated by transition-metal systems prompted the question: can FLP reactivity be extended to dinitrogen? A major challenge in such efforts is the paucity of main group systems known to capture N_2 . While the adduct $(\text{N}_2)\text{BF}_3$ was reportedly generated via supersonic expansion at 600 torr and 170 K²⁵ in 1978, it has only been recently shown that a CAAC-stabilised borylene was used to effect the first metal-free capture of N_2 by Braunschweig and coworkers.²⁶⁻²⁷

A computational study by Frenking et al. described the compound $\text{Ph}_3\text{PNNPPH}_3$ ²⁸ as a N_2 unit stabilised by two phosphine donors.²⁹ While this discussion is thought provoking, it is important to note that this species only liberates N_2 under thermal duress. In our own efforts towards FLP- N_2 chemistry, we began an examination of the chemistry diazomethanes with boranes. Diazomethanes are isolable yet liberate N_2 , and the Frenking logic allows us to view these species as carbene-stabilized- N_2 complexes.³⁰

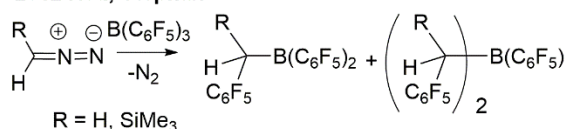
1996 Metzler, Denk



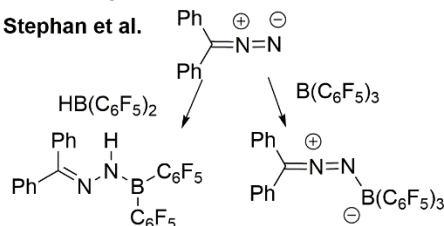
2005 Soderquist



2012 Neu, Stephan



2017 Stephan et al.



Scheme 1 Reactions of silylene and diazomethanes with boranes.

In considering the reactions of diazomethanes with electrophilic boranes, we noted that Brown *et al.*,³¹ described the polymerisation of diazomethane by BF_3 . Brown also suggested that reactions of dialkylchloroboranes with diazoacetates results in chloride or alkyl group migration to the diazomethane carbon.³² In a related sense, Soderquist et al. exploited the reactions of $\text{Me}_3\text{SiCH(N}_2\text{)}$ with 9-borabicyclononanes to give 10- Me_3Si -9-borabicyclodecane (Scheme 1)³³ while Shea and Bai described the synthesis of $(\text{Me}_3\text{SiCH}_2)_3\text{B}$ from $(\text{Me}_2\text{S-BH}_3)$ and $\text{Me}_3\text{SiCHN}_2$.³⁴ In 2012 and 2013, we built on these precedents to react diazomethanes with a variety of electrophilic boranes, effecting insertion of carbene fragments

into B-C bonds with liberation of N₂ (Scheme 1).³⁵ In a related reaction, the *bis*(amino)silylene inserts into a B-C bond of B(C₆F₅)₃ affording (HCN*t*Bu)₂Si(C₆F₅)(B(C₆F₅)₂) (Scheme 1).³⁶⁻³⁷ More recently, we employed the sterically-encumbered diazomethane Ph₂CN₂ in reactions with HB(C₆F₅)₂ and B(C₆F₅)₃.³⁸ In the former case, 1,1-hydroboration afforded Ph₂CNNH(B(C₆F₅)₂) while reaction with B(C₆F₅)₃ provided the thermally unstable diazomethane adduct Ph₂CNNB(C₆F₅)₃ (Scheme 1).³⁹⁻⁴⁰

In this paper, we explore the reactions of phosphine-diazomethane adducts with B(C₆F₅)₃. Herein, we show that the phosphine-diazomethane adducts do not effect insertion of carbene into B-C bonds. Rather phosphine-diazomethane adducts are shown to bind B(C₆F₅)₃ reversibly, and to react subsequently with proton sources. These reactions demonstrate differing sites for Lewis and Brønsted reactivity.

Results and Discussion

Since the original report by Staudinger and Meyer,⁴¹ literature studies⁴²⁻⁴⁸ have probed the reactions of diazomethanes with phosphine donors. In a similar fashion, we have probed the addition of Ph₃P to a solution of EtOC(=O)CH(N₂) to afford a pale yellow solution from which crystals were isolated of the product **1** in 86% yield. The ³¹P{¹H} NMR spectrum showed a singlet at 22.7 ppm. In addition, the ¹H and ¹³C{¹H} NMR data were consistent with the literature description of EtOC(=O)CH(NNPPH₃). These data are consistent with the previous report of compound **1**.⁴⁴ The structure of **1** was also confirmed via X-ray methods. The structure reveals a pseudo-tetrahedral geometry at phosphorus with a P-N bond distance of 1.621(3) Å while the N-N and N-C bond distances are 1.364(3) Å and 1.293(4) Å, respectively. The corresponding P-N-N and N-N-C angles are 111.8(2)° and 114.2(2)°, respectively. These metric parameters are similar to those found in the previously reported structures of EtCO₂CH=CMe(EtOC(=O)C(NNPPH₃)) and MeCO₂CH=C(CF₃)(MeC(=O)C(NNPPH₃)).⁴⁶

The corresponding reactions of Cy₃P and *t*Bu₃P with EtOC(=O)CH(N₂) also afforded pale yellow solutions. These solutions exhibited ³¹P{¹H}, NMR signals at 41.7 and 53.1 ppm, respectively while the ¹H and ¹³C{¹H} NMR were consistent with the formulation these products as EtOC(=O)CH(NNPR₃) (R = Cy **2** and *t*Bu **3**) (Scheme 2). In the case of **2** a pale-yellow solid was isolable in 70% yield, whereas for **3**, its oily nature precluded isolation as a pure solid. The structure of **2** was also confirmed crystallographically (Figure 2) revealing P-N, N-N and N-C bond distances of 1.6368(17) Å, 1.339(2) Å and 1.297(3) Å, respectively. The corresponding N-N-P and N-N-C angles were determined to be 112.4(1)° and 117.3(2)°, respectively.

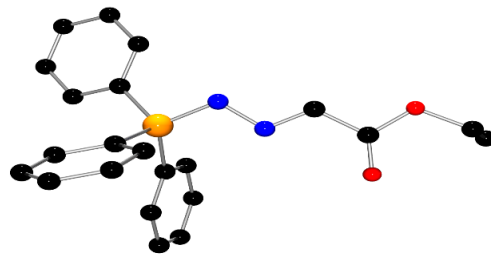


Figure 1 POV-ray depiction of **1**, hydrogen atoms are omitted for clarity. C: black, P: orange, N: blue, O: red.

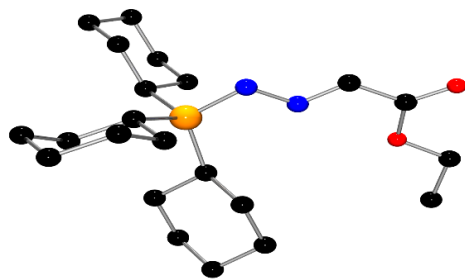


Figure 2 POV-ray depiction of **2**, hydrogen atoms are omitted for clarity. C: black, P: orange, N: blue, O: red.

DFT calculations using Gaussian 16 using the BP86 functional and the def2-TZVPP basis set were performed on the optimised structures of **1-3**. The HOMOs for these molecules were centred on the nitrogen atoms comprised primarily of the lone pairs on these atoms. The HOMO-1s which were 3.0, 1.9, and 3.9 Kcal/mol lower in energy than the HOMOs for **1**, **2**, and **3**, respectively and have components on the P-N and N-C fragments. The HOMO-2s, which are 19.2, 21.0, and 22.5 Kcal/mol lower in energy than the HOMOs for **1**, **2**, and **3**, respectively, are centred on the ester-carbonyl oxygen atoms and thus ascribed to a lone pair of electrons on oxygen (Figure 3). It is also interesting to note that these molecules exhibit stronger N-N and weaker P-N bonds than that seen in Ph₃PNNPPH₃²⁹ (see SI).

Addition of B(C₆F₅)₃ to solutions of **1-3** were performed in CDCl₃ at -45 °C. After 30 minutes of stirring the solutions were warmed to room temperature. In the case of **1**, the mixture appears to be an equilibrium as evidenced by the broadened resonances in the ¹¹B{¹H} and ³¹P{¹H} NMR spectra. This suggests the formation of a weak adduct **4** between **1** and B(C₆F₅)₃. Efforts to isolate **4** for further characterisation were unsuccessful as on warming to room temperature the product of para-attack, Ph₃PC₆F₄BF(C₆F₅)₂⁴⁹ precipitates from solution. In contrast, reaction of **2** with B(C₆F₅)₃ prompted was a downfield shift of the ³¹P{¹H} NMR resonance to 45.4 ppm. The central carbon of the diazomethane fragment exhibits a doublet at 125.4 ppm with a coupling constant of 49 Hz. The corresponding CH shows a singlet resonance in the ¹H NMR spectrum at 7.10 ppm. The corresponding ¹¹B{¹H} NMR resonance at -1.36 ppm together with the ¹⁹F{¹H} NMR signals at -134.2, -159.1 and -165.0 ppm are consistent with a four coordinate boron centre and suggesting the formulation of the Lewis acid-base adduct, EtOC(=O)B(C₆F₅)₃CH(NNPCy₃) **5** (Scheme 2). In a similar fashion addition of B(C₆F₅)₃ to **3** afforded

the analogous adduct $\text{EtOC(=O(B(C}_6\text{F}_5)_3))CH(NNPtBu_3)$ **6** (Scheme 2) which exhibited spectroscopic parameters that were similar to those seen for **5** (see SI). In this latter case, crystals of **6** were obtained and the crystallographic study confirmed the formation of a borane adduct of **3** at the carbonyl oxygen affording **6** (Figure 4). The B-O distance was determined to be 1.555(5) Å while the P-N, N-N and N-C distances were found to be 1.668(3) Å, 1.329(4) Å and 1.325(5) Å, respectively. The slightly longer P-N distance in **6** compared to **1** and **2** is attributed to the steric bulk of $t\text{Bu}_3\text{P}$.

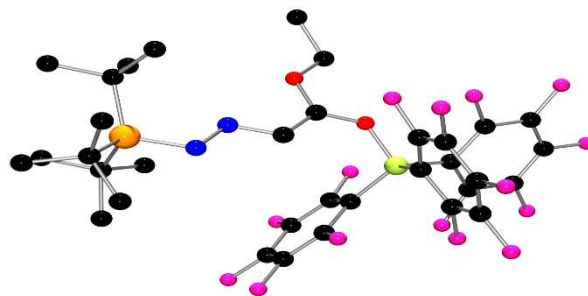


Figure 4 POV-ray depiction of **6**, hydrogen atoms are omitted for clarity. C: black, P: orange, N: blue, O: red; B: yellow-green; F: pink.

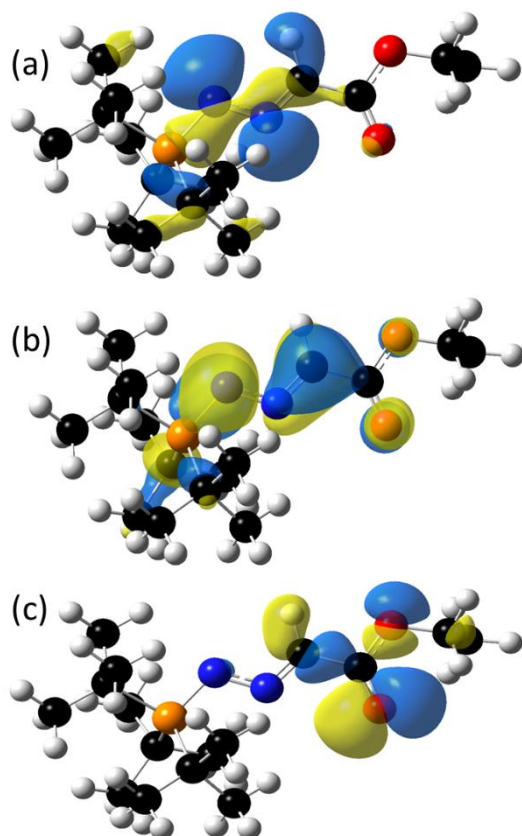
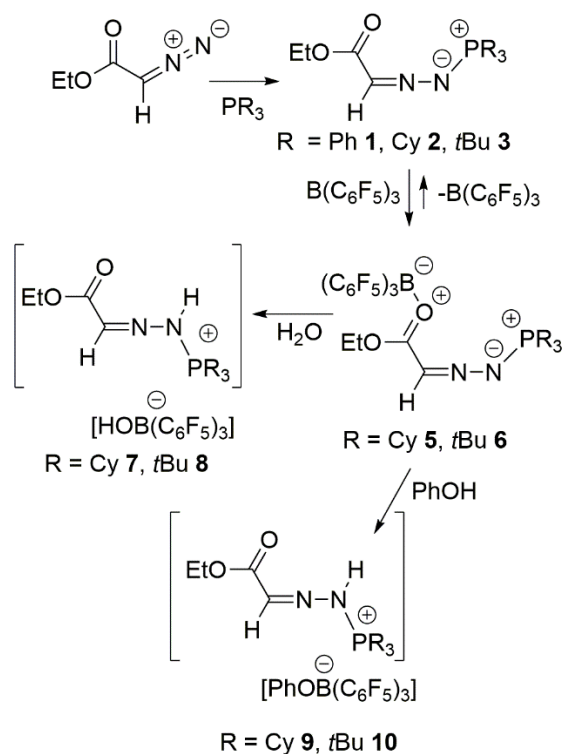


Figure 3 Surface contour plots (isovalue 0.03) of the (a) HOMO, (b) HOMO-1 (c) HOMO-2 computed for **3** computed at the BP86/def2-TZVPP level of theory.

The binding of borane to the carbonyl oxygen atom in **5** and **6** is perhaps surprising given the HOMO of **3** is centred on the nitrogen atoms (see above). On the other hand, while the HOMO-2 located on the carbonyl oxygen atom is 22.5 Kcal/mol lower than the HOMO in energy, it is also in a significantly less hindered site. Thus, it appears binding of the phosphines $t\text{Bu}_3\text{P}$ and Cy_3P sterically precludes binding of $\text{B(C}_6\text{F}_5)_3$ to either nitrogen, favouring binding to the less sterically encumbered carbonyl oxygen atom.

It is also interesting that the adducts **5** and **6** are formed and that the initial addition of phosphine precludes the direct reaction of the diazomethane with $\text{B(C}_6\text{F}_5)_3$ as previously reported.^{35, 37} In more recent work we have shown that adducts are accessible for sterically hindered diazomethanes,³⁸ but for less encumbered reagents, loss of N_2 is facile and insertion of the carbene fragment into the B-C bond proceeds rapidly.^{35, 37} The present result suggests that P-N binding is favoured over B-N bonding, inferring that the N_2 fragment of the diazomethane is a better electron acceptor than donor.



Scheme 2 Synthetic pathways to **1-10**.

Compounds **5** and **6** were found to be thermally stable but did react with water. Indeed, slow stoichiometric addition of H_2O to **5** afforded a new species **7**. The ^1H NMR spectrum revealed a broad resonance at 11.88 ppm in addition to the expected signals. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed a signal at 57.2 ppm, while the $^{19}\text{F}\{^1\text{H}\}$ NMR resonances at -135.60, -160.88 and -165.15 ppm in addition to the $^{11}\text{B}\{^1\text{H}\}$ signal at -3.84 ppm, were consistent with the formulation of **7** as $[\text{EtOC(=O)CHNNHPCy}_3][\text{HO(B(C}_6\text{F}_5)_3)]$ (Scheme 2). The corresponding reaction with **6** gave rise to a new species **8** that

showed the analogous ^1H NMR doublet resonance at 11.20 ppm with a P-H coupling constant of 25.4 Hz. The $^{31}\text{P}\{^1\text{H}\}$ NMR signal at 72.90 ppm, the $^{19}\text{F}\{^1\text{H}\}$ signals at -135.55, -160.99 and -165.27, together with the $^{11}\text{B}\{^1\text{H}\}$ NMR resonance at -3.84 ppm led to the formulation of **8** as $[\text{EtOC(=O)CHNNHP}t\text{Bu}_3][\text{HOB(C}_6\text{F}_5)_3]$ (Scheme 2). This was confirmed unambiguously by X-ray crystallography (Figure 5). The anion of **8** exhibited the expected pseudo-tetrahedral geometry about boron and the resulting B-OH distance in the anion was found to be 1.484(3) Å. The oxygen atom is oriented 2.153 Å from the proton on the N alpha to the phosphorus atom in the solid-state, indicative of hydrogen-bonding. Protonation of the N-atom has little impact on the P-N and N-N distances, as they were determined to be 1.661(2) Å and 1.381(3) Å,

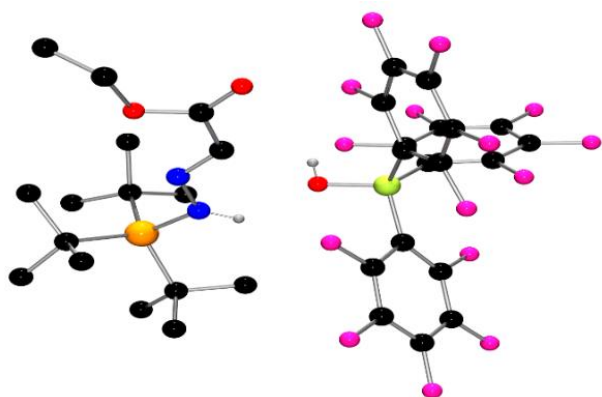


Figure 5 POV-ray depiction of **8**, hydrogen atoms are omitted for clarity. C: black, P: orange, N: blue, O: red; B: yellow-green; F: pink.

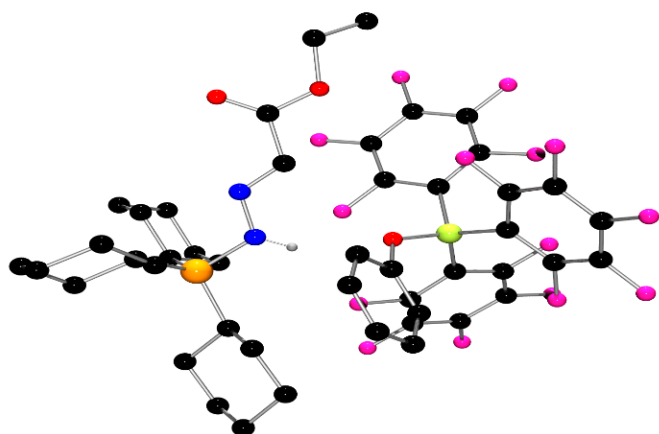


Figure 6 POV-ray depiction of **9**, hydrogen atoms are omitted for clarity. C: black, P: orange, N: blue, O: red; B: yellow-green; F: pink.

respectively, although the resulting N-C distance in **8** is 1.271(3) Å, which is significantly shorter than that in **6**.

In a similar fashion, compound **5** was seen to react with phenol at -45 °C in 30 minutes. The solution became colourless and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum exhibited a broad singlet at 60.4 ppm, attributable to a new species **9**. The corresponding $^{11}\text{B}\{^1\text{H}\}$ NMR signal was observed at -2.6 ppm while the $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum showed signals at -133.9, 160.9, and -165.8 ppm. These latter data were consistent with the presence of the four-

coordinate boron anion $[\text{PhOB(C}_6\text{F}_5)_3]^-$. The ^1H NMR spectrum revealed a doublet at 8.86 ppm with a P-H coupling constant of 24.2 Hz attributable to an NH proton. $^{13}\text{C}\{^1\text{H}\}$ NMR data revealed a doublet at 141.6 ppm with a coupling constant of 14.1 Hz. Collectively these data infer a formulation of **9** as $[\text{EtOC(=O)CHNNHPCy}_3][\text{PhOB(C}_6\text{F}_5)_3]$ (Scheme 2). Similar reaction of **6** with phenol in CH_2Cl_2 at -45 °C afforded the corresponding product **10** as evidenced by the $^{31}\text{P}\{^1\text{H}\}$ signal at 74.0 ppm, and the $^{11}\text{B}\{^1\text{H}\}$ and $^{19}\text{F}\{^1\text{H}\}$ NMR signals indicative of the formation of the four-coordinate boron anion $[\text{PhOB(C}_6\text{F}_5)_3]^-$. The ^1H NMR doublet at 8.26 ppm with a P-H coupling constant of 24.2 Hz attributable to an NH proton together with the $^{13}\text{C}\{^1\text{H}\}$ signal at 141.1 ppm were consistent with the formation of **10** as $[\text{EtOC(=O)CHNNHP}t\text{Bu}_3][\text{PhOB(C}_6\text{F}_5)_3]$ (Scheme 2). The formulation of compound **9** were confirmed by a crystallographic study of **9** (Figure 6). The anion $[\text{PhOB(C}_6\text{F}_5)_3]^-$ was unexceptional with a B-O distance of 1.504(2) Å while the cation in **9** was analogous to that seen in **8**.

The formation of **7-10** illustrate that the species **5** and **6** establish equilibrium access to free $\text{B(C}_6\text{F}_5)_3$ and **2** and **3**, respectively. This permits the Lewis acid to bind water or phenol, resulting in an increase in acidity and prompting protonation of the alpha nitrogen atom of **2** or **3**, affording the resulting observed salts. Protonation at the alpha nitrogen is consistent with the computed HOMOs and illustrates the contrasting reactivity of **2** and **3** with Lewis and Brønsted acids.

Conclusion

The present results demonstrate that addition of phosphine to diazomethanes leads to the formation of the phosphine-diazomethane adducts **1-3**. Upon addition of borane, these adducts preclude insertion into B-C bonds but rather can form Lewis acid-base adducts **5** and **6** at the carbonyl-oxygen. In contrast, in subsequent reactions with H_2O or phenol, these species exhibit Brønsted acidity at the nitrogen atom adjacent phosphorus, affording the salts **7-10**. This contrasting Lewis and Brønsted reactivity provides an interesting example of the impact of steric demands. Further studies of the reactions of diazomethanes with FLPs continues in our laboratories, targeting applications in organic synthesis and in the modelling of main group N_2 chemistry.

Experimental Section

General Considerations: All manipulations were carried out under an atmosphere of dry, O_2 -free N_2 conditions in a VAC glovebox. All glass devices used for the synthesis were oven-dried and cooled under vacuum before use. Oxygen-free and dry solvents were prepared using an Innovative Technologies solvent purification system. Deuterated chloroform (CDCl_3) purchased from Cambridge Isotope Laboratories Inc. was degassed and stored over molecular sieves (4 Å) for at least two days prior to use. Commercial reagents were used without further purification unless indicated otherwise. $\text{B(C}_6\text{F}_5)_3$ was purchased from Boulder Scientific and sublimed under vacuum at 85 °C prior to use. NMR spectra were recorded at room temperature (298K) unless otherwise mentioned on a Bruker

Avance III 400 MHz, an Agilent DD2 500, and an Agilent DD2 700 Spectrometers. Spectra were referenced to the residual solvent signals (CDCl_3 : ^1H = 7.26 ppm and ^{13}C = 77.2 ppm). Chemical shifts (δ) are reported in ppm and coupling constants (J) are listed as absolute values in Hz. Multiplicities are reported as singlet (s), doublet (d), triplet (t), multiplet (m), overlapping (ov), and broad (br). Medium-High-resolution mass spectra (MHR-MS) were obtained on a Agilent 6538 UHD mass spectrometer.

Synthesis of $\text{EtOC(=O)CH(NNPR}_3\text{)}$ ($\text{R} = \text{Ph } \mathbf{1}$, $\text{Cy } \mathbf{2}$, $\text{tBu } \mathbf{3}$) These products were prepared in a similar fashion and thus only one preparation is detailed. In the case of **1**, this is a minor modification of a literature procedure.⁴⁴ A 20 mL vial was charged with Ph_3P (0.100g, 0.392 mmol) in pentane (5 mL) and a solution of $\text{EtOC(=O)CH(N}_2\text{)}$ (0.050 g) in pentane (0.5 mL) was added, in a dropwise fashion. The resulting pale-yellow solution was stored in the glovebox and crystals precipitated over the next 4 hours. The solvent was carefully decanted and the solid was dried *in vacuo* to give a white to pale yellow solid, 0.142 g (86%). **1**: ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 7.77 (d, $^4J_{\text{H-P}} = 2.3$ Hz, 1H, CH), 7.71 – 7.42 (m, 15H, (C_6H_5)₃), 4.20 (q, $^3J_{\text{H-H}} = 7.1$ Hz, 2H, CH_2), 1.27 (t, $^3J_{\text{H-H}} = 7.1$ Hz, 3H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 298 K): δ 165.6 (s, C=O), 138.3 (d, $^3J_{\text{C-P}} = 47.9$ Hz, N-CH), 133.7 (d, $^2J_{\text{C-P}} = 8.4$ Hz, *o*-(C_6H_5)₃), 132.6 (d, $^4J_{\text{C-P}} = 2.9$ Hz, *p*-(C_6H_5)₃), 128.9 (d, $^3J_{\text{C-P}} = 11.8$ Hz, *m*-(C_6H_5)₃), 127.9 (d, $^1J_{\text{C-P}} = 93.9$ Hz, P-qC), 59.8 (s, CH_2), 14.6 (s, CH_3) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , 298 K): δ 22.7 (s) ppm. MHR-MS (ESI+): calculated for $\text{C}_{22}\text{H}_{21}\text{N}_2\text{O}_2\text{P}$: 376.13; found $\text{C}_{22}\text{H}_{21}\text{N}_2\text{O}_2\text{P}$: 377.14 (+ H^+).

2: pale yellow solid 0.108 g (70%); ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 7.46 (d, $^4J_{\text{H-P}} = 1.7$ Hz, 1H, N-CH), 4.19 (q, $^3J_{\text{H-H}} = 7.1$ Hz, 2H, CH_2), 2.35 – 2.24 (m, 3H, P-CH), 1.95 (d, $^3J_{\text{H-H}} = 12.8$ Hz, 6H, C_6H_{11}), 1.88 – 1.79 (m, 6H, C_6H_{11}), 1.74 (bs, 3H, C_6H_{11}), 1.53 (q, $^3J_{\text{H-H}} = 11.8$ Hz, 6H, C_6H_{11}), 1.32 – 1.21 (m, 12H, CH_3 and C_6H_{11}) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 298 K): δ 166.3 (s, C=O), 133.3 (d, $^3J_{\text{C-P}} = 44.0$ Hz, N-CH), 59.3 (s, CH_2), 33.2 (d, $^1J_{\text{C-P}} = 51.1$ Hz, P-CH), 27.2 (d, $^2J_{\text{C-P}} = 10.9$ Hz, C_6H_{11}), 26.8 (d, $^3J_{\text{C-P}} = 3.5$ Hz, C_6H_{11}), 26.2 (d, $^4J_{\text{C-P}} = 1.4$ Hz, C_6H_{11}), 14.7 (s, CH_3) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , 298 K): δ 41.7 (s) ppm. MHR-MS (ESI+): calculated for $\text{C}_{22}\text{H}_{39}\text{N}_2\text{O}_2\text{P}$ 394.27; found for $\text{C}_{22}\text{H}_{39}\text{N}_2\text{O}_2\text{P}$ 395.28 (+ H^+).

3: Yield (NMR): 98%; ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 7.42 (s, 1H, N-CH), 4.17 (q, $^3J_{\text{H-H}} = 7.1$ Hz, 2H, CH_2), 1.48 (d, $^3J_{\text{H-P}} = 12.5$ Hz, 27H, 9 CH_3 , tBu_3), 1.24 (t, $^3J_{\text{H-H}} = 7.1$ Hz, 3H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 298 K): δ 166.6 (s, C=O), 132.51 (d, $^3J_{\text{C-P}} = 44.4$ Hz, N-CH), 59.2 (s, CH_2), 40.5 (d, $^1J_{\text{C-P}} = 38.9$ Hz, P-qC (tBu_3)), 30.0 (s, 9 CH_3 (tBu_3)), 14.6 (s, CH_3) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , 298 K): δ 53.1 (s) ppm. MHR-MS (ESI+, CDCl_3) calculated for $\text{C}_{16}\text{H}_{33}\text{N}_2\text{O}_2\text{P}$: 316.23; found for $\text{C}_{16}\text{H}_{33}\text{N}_2\text{O}_2\text{P}$: 317.2357 (+ H^+)

Synthesis of $\text{EtOC(=O)CH(NNPR}_3\text{)}(\text{B(C}_6\text{F}_5\text{)}_3)$ ($\text{R} = \text{Cy } \mathbf{5}$, $\text{tBu } \mathbf{6}$) These products were prepared in a similar fashion and thus only one preparation is detailed. A 20 mL vial was charged with **2** (0.031 g, 0.078 mmol) in CDCl_3 (0.4 mL). The reaction was cooled to -45°C and a pre-cooled solution of $\text{B(C}_6\text{F}_5\text{)}_3$ (0.040 g, 0.078 mmol), in CDCl_3 (0.3 mL), was added in a dropwise fashion. The resulting yellow solution was stirred at -45°C for a period of 30

minutes and was warmed to room temperature. These compounds proved to be highly sensitive and all attempts at isolation led to hydrolysis. **5**: Yield (NMR): 98%; ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 7.10 (s, 1H, N-CH), 4.36 (q, $^3J_{\text{H-H}} = 7.1$ Hz, 2H, CH_2), 2.40 – 2.24 (m, 3H, P-CH), 1.90 – 1.80 (m, 12H, *o*- C_6H_{11}), 1.77 (s, 3H, *p*- C_6H_{11}), 1.48 – 1.36 (m, 6H, *m*- C_6H_{11}), 1.31 (t, $^3J_{\text{H-H}} = 7.1$ Hz, 3H, CH_3), 1.28 – 1.22 (m, 9H, C_6H_{11}) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 298 K): δ 172.8 (s, C=O), 149.14 (bs, C_6F_5), 146.8 (bs, C_6F_5), 138.19 (bs, C_6F_5), 135.7 (bs, C_6F_5), 125.4 (d, $^3J_{\text{C-P}} = 48.8$ Hz, N-CH), 66.0 (s, CH_2), 32.6 (d, $^1J_{\text{C-P}} = 48.1$ Hz, P-CH), 26.9 (d, $^2J_{\text{C-P}} = 11.2$ Hz, C_6H_{11}), 26.1 (d, $^3J_{\text{C-P}} = 3.8$ Hz, C_6H_{11}), 25.9 (s, C_6H_{11}), 14.1 (s, CH_3) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , 298 K): δ 45.4 (s) ppm. $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3 , 298 K): δ -134.2 (d, $^3J_{\text{F-F}} = 21.5$ Hz, 6F, *o*- C_6F_5), -159.1 (t, $^3J_{\text{F-F}} = 20.2$ Hz, *p*- C_6F_5), -165.0 (bt, $^3J_{\text{F-F}} = 20.2$ Hz, *m*- C_6F_5) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3 , 298 K): δ -1.4 (bs) ppm.

6: Yield (NMR): 99%; ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 7.07 (s, 1H, N-CH), 4.37 (q, $^3J_{\text{H-H}} = 7.1$ Hz, 2H, CH_2), 1.44 (d, $^3J_{\text{H-P}} = 12.8$ Hz, 27H, 9 CH_3 (tBu_3)), 1.30 (t, $^3J_{\text{H-H}} = 7.1$ Hz, 3H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 298 K): δ 172.9 (s, C=O), 149.1 (bm, C_6F_5), 148.7 (bm, C_6F_5), 140.9 (m, C_6F_5), 138.3 (bm, C_6F_5), 135.8 (bm, C_6F_5), 125.8 (d, $^3J_{\text{C-P}} = 45.3$ Hz, N-CH), 119.1 (bm, C_6F_5), 65.9 (s, CH_2), 40.8 (d, $^1J_{\text{C-P}} = 35.0$ Hz, P-qC), 29.7 (s, 9 CH_3 (tBu_3)), 14.1 (s, CH_3) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , 298 K): δ 55.2 (s) ppm. $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3 , 298 K): δ -134.2 (d, $^3J_{\text{F-F}} = 20.0$ Hz, *o*- C_6F_5), -159.1 (bs, *p*- C_6F_5), -165.0 (bs, *m*- C_6F_5) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3 , 298 K): δ -1.3 (bs) ppm.

Synthesis of $[\text{EtOC(=O)CHNNHPR}_3][\text{HOB(C}_6\text{F}_5\text{)}_3]$ ($\text{R} = \text{Cy } \mathbf{7}$, $\text{tBu } \mathbf{8}$) These products were prepared in a similar fashion and thus only one preparation is detailed. To the 20 mL vial with a pre-cooled (-45°C) solution of **5** (0.078 mmol) degassed H_2O was added (0.3 mL). The water freezes immediately and the ice containing solution was stirred for 10 min before it was allowed to warm to room temperature. As the ice started to melt. The mixture was stirred for further 30 min while the solution becomes colourless. **7**: Yield (NMR): 97%; ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 11.88 (bs, 1H, NH), 7.27 (s, 1H, N-CH), 4.21 (q, $^3J_{\text{H-H}} = 7.1$ Hz, 2H, CH_2), 2.53 (bs, 1H, OH), 2.42 (q, $J = 12.3$ Hz, 3H, qC, C_6H_{11}), 1.91 – 1.76 (m, 15H, C_6H_{11}), 1.52-1.41 (m, 6H, C_6H_{11}), 1.31 – 1.20 (m, 12H, 3H CH_3 , 9H C_6H_{11}) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 298 K): δ 162.3 (s, C=O), 149.2 (bs, C_6F_5), 146.9 (bs, C_6F_5), 139.6 (d, $^3J_{\text{C-P}} = 16.2$ Hz, N-CH), 137.9 (bs, C_6F_5), 135.6 (bs, C_6F_5), 61.4 (s, CH_2), 32.1 (d, $^1J_{\text{C-P}} = 48.7$ Hz, P-CH), 26.5 (d, $^2J_{\text{C-P}} = 12.6$ Hz, C_6H_{11}), 26.2 (d, $^3J_{\text{C-P}} = 3.4$ Hz, C_6H_{11}), 25.5 (s, C_6H_{11}), 14.02 (s, CH_3) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , 298 K): δ 57.2 (bs) ppm. $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3 , 298 K): δ -135.6 (d, $^3J_{\text{F-F}} = 19.2$ Hz, *o*- C_6F_5), -160.9 (t, $^3J_{\text{F-F}} = 20.3$ Hz, *p*- C_6F_5), -165.2 (t, $^3J_{\text{F-F}} = 18.6$ Hz, *m*- C_6F_5) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3 , 298 K): δ -3.8 (bs) ppm. MHR-MS (ESI+, CDCl_3) calculated for $\text{C}_{22}\text{H}_{40}\text{N}_2\text{O}_2\text{P}^+$: 395.28; found for $\text{C}_{22}\text{H}_{40}\text{N}_2\text{O}_2\text{P}^+$: 395.28; MHR-MS (ESI-, CDCl_3) calculated for $\text{C}_{18}\text{HBF}_{15}\text{O}^-$: 528.99; found for $\text{C}_{18}\text{HBF}_{15}\text{O}^-$: 528.94.

8: Yield (NMR): >99%; ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 11.20 (d, $^2J_{\text{H-P}} = 25.4$ Hz, 1H, NH), 7.65 (s, 1H, N-CH), 4.19 (q, $^3J_{\text{H-H}} = 7.1$ Hz, 2H, CH_2), 2.76 (bs, 1H, OH), 1.55 (d, $^3J_{\text{H-P}} = 14.6$ Hz, 27H, tBu_3), 1.26 (t, $^3J_{\text{H-H}} = 7.1$, 3H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz,

CDCl₃, 298 K): δ 162.2 (s, C=O), 149.2 (bs, C₆F₅), 146.9 (bs, C₆F₅), 140.2 (d, $^3J_{C-P}$ = 13.9 Hz, N-CH), 137.8 (bs, C₆F₅), 135.6 (bs, C₆F₅), 61.5 (s, CH₂), 41.5 (d, $^1J_{C-P}$ = 34.3 Hz, qC, tBu₃), 29.5 (s, 9Me, tBu₃), 13.9 (s, CH₃) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl₃, 298 K): δ 72.9 (bs) ppm. $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl₃, 298 K): δ -135.6 (d, $^3J_{F-F}$ = 19.4 Hz, o-C₆F₅), -161.0 (t, $^3J_{F-F}$ = 19.7 Hz, p-C₆F₅), -165.3 (t, $^3J_{F-F}$ = 18.6 Hz, m-C₆F₅) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl₃, 298 K): δ - 3.8 (bs) ppm. MHR-MS (ESI+, CDCl₃) calculated for C₁₆H₃₄N₂O₂P⁺: 317.24; found for C₁₆H₃₄N₂O₂P⁺: 317.24; MHR-MS (ESI-, CDCl₃) calculated for C₁₈HBF₁₅O⁻: 528.99; found for C₁₈HBF₁₅O⁻: 529.01.

Synthesis of [EtOC(=O)CHNNHPR₃][PhOB(C₆F₅)₃] (R = Cy 9, tBu 10)

These products were prepared in a similar fashion and thus only one preparation is detailed. To the 20 mL vial with the reaction product of EtOC(OB(C₆F₅)₃)CHNNPCy₃ (0.071 g, 0.078 mmol) a solution of phenol (0.007 g, 0.078 mmol), diluted in CDCl₃ (0.3 mL) was added, in a dropwise fashion. The yellow solution was stirred at -45 °C for a period of 30 minutes and turned to a colourless solution over time. **9**: Yield (NMR): 98%; ^1H NMR (400 MHz, CDCl₃, 298 K): δ 8.86 (bs, 1H, NH), 7.83 (s, 1H, CH), 6.94 (t, $^3J_{H-H}$ = 7.8 Hz, 2H, C₆H₅), 6.69 – 6.59 (m, 3H, C₆H₅), 4.21 (q, $^3J_{H-H}$ = 7.1 Hz, 2H, CH₂), 2.47 (q, $^2J_{H-P}$ = 12.5, 2.8 Hz, 3H, P-CH), 1.88 – 1.71 (m, 15H, C₆H₁₁), 1.52–1.39 (m, 6H, C₆H₁₁), 1.29 – 1.19 (m, 12H, 3H CH₃, 9H C₆H₁₁) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl₃, 298 K): δ 161.9 (s, C=O), 159.7 (s, qC-O), 149.2 (bs, C₆F₅), 146.8 (bs, C₆F₅), 141.6 (d, $^3J_{C-P}$ = 14.1 Hz, N-CH), 140.1 (bs, C₆F₅), 138.0 (m, C₆F₅), 135.5 (m, C₆F₅), 129.8 (s, C₆H₅), 128.8 (s, C₆H₅), 119.9 (s, C₆H₅), 119.7 (s, C₆H₅), 115.4 (s, C₆H₅), 61.6 (s, CH₂), 32.1 (d, $^1J_{C-P}$ = 47.7 Hz, P-CH), 26.7 (d, $^2J_{C-P}$ = 12.8 Hz, C₆H₁₁), 26.0 (d, $^3J_{C-P}$ = 3.3 Hz, C₆H₁₁), 25.4 (bs, C₆H₁₁), 13.9 (s, CH₃) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl₃, 298 K): δ 60.4 (s) ppm. $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl₃, 298 K): δ -133.9 (d, $^3J_{F-F}$ = 23.6 Hz, o-C₆F₅), -160.9 (t, $^3J_{F-F}$ = 20.4 Hz, p-C₆F₅), -165.8 (bt, $^3J_{F-F}$ = 24.5 Hz, m-C₆F₅) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl₃, 298 K): δ - 2.6 (s) ppm. MHR-MS (ESI+, CDCl₃) calculated for C₂₂H₄₀N₂O₂P⁺: 395.28; found for C₂₂H₄₀N₂O₂P⁺: 395.28.

10: Yield (NMR): >99%; ^1H NMR (400 MHz, CDCl₃, 298 K): δ 8.26 (d, $^2J_{H-P}$ = 24.2 Hz, 1H, NH), 7.80 (s, 1H, CH), 6.97 – 6.92 (m, 2H, C₆H₅), 6.68 – 6.57 (m, 3H, C₆H₅), 4.19 (q, $^3J_{H-H}$ = 7.1 Hz, 2H, CH₂), 1.56 (d, $^3J_{H-P}$ = 14.9 Hz, 27H, tBu₃), 1.27 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH₃) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl₃, 298 K): δ 161.8 (s, C=O), 160.3 (s, C-O), 149.3 (bs, C₆F₅), 146.8 (bs, C₆F₅), 141.1 (d, $^3J_{C-P}$ = 12.3 Hz N-CH), 140.0 (bs, C₆F₅), 137.8 (bs, C₆F₅), 135.5 (bs, C₆F₅), 128.8 (s, C₆H₅), 119.7 (s, C₆H₅), 119.0 (s, C₆H₅), 61.8 (s, CH₂), 41.6 (d, $^1J_{C-P}$ = 33.1 Hz, qC, tBu₃), 29.3 (s, 9Me, tBu₃), 13.8 (s, CH₃) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl₃, 298 K): δ 74.0 (bs) ppm. $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl₃, 298 K): δ -133.4 (d, $^3J_{F-F}$ = 21.5 Hz, o-C₆F₅), -161.2 (t, $^3J_{F-F}$ = 20.4 Hz, p-C₆F₅), -165.9 (bt, $^3J_{F-F}$ = 20.3 Hz, m-C₆F₅) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl₃, 298 K): δ - 2.8 (s) ppm. MHR-MS (ESI+, CDCl₃) calculated for C₁₆H₃₄N₂O₂P⁺: 317.24; found for C₁₆H₃₄N₂O₂P⁺: 317.24.

Computational Details Electronic structure calculations, including geometry optimisation, frequency calculations, and energy calculations, were performed using Gaussian 16⁵⁰ using the BP86 functional and the def2-TZVPP basis set.⁵⁰⁻⁵³ Natural bond orbital and natural population analyses were performed

on optimised structures using NBO 6.0.⁵⁴ X-ray coordinates were used as the starting geometries. The Cartesian coordinates of the optimised structures are collected in tables 1-4. The absence of any imaginary frequency with an absolute magnitude greater than 10 cm⁻¹ confirmed that each optimised structure was indeed located at a minimum on its potential energy hypersurface.

X-ray Diffraction Studies: Single crystals were coated with paratone oil, mounted on a cryoloop and frozen under a stream of cold nitrogen. Data were collected on a Bruker Apex2 X-ray diffractometer at 150(2) K for all crystals using graphite monochromated Mo-K α radiation (0.71073 Å). Data were collected using Bruker APEX-2 software and processed using SHELX and an absorption correction applied using multi-scan within the APEX-2 program. All structures were solved and refined by direct methods within the SHELXTL package. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

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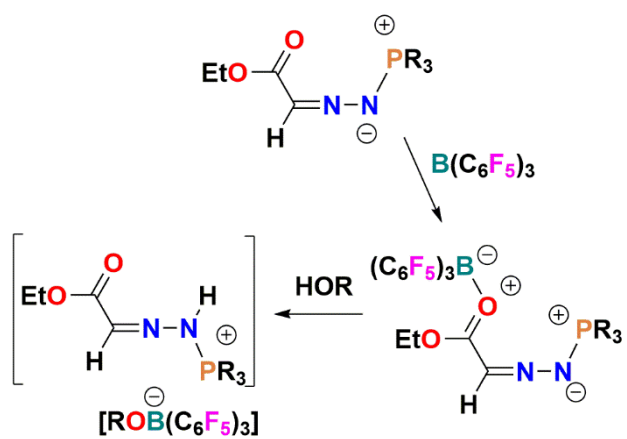
Conflicts of interest

There are no conflicts to declare.

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